ROTATIONAL ENERGY TRANSFER AND DEPOLARIZATION IN RARE GAS + CN ($\tilde{X}$, v=0) COLLISIONS

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Rotational energy transfer and depolarization rates have been determined for fine-structure-selected rotational levels of the vibrationless ground state of CN ($\tilde{X}\ ^2\Sigma^+$) radicals. Collisions with Ar, He and the photolytic precursor, CH_3COCN have been studied with polarized transient frequency modulation (FM) absorption spectroscopy. Transient FM signals were recorded as a function of probe laser detuning across Doppler-broadened lines of the $\tilde{A}-\tilde{X}$ $(1-0)$ band, monitoring the saturation recovery kinetics after a tunable dye laser pulse selectively bleached the probed CN rotational level. The refilling kinetics of a hole in an otherwise thermalized state distribution is identical to the hypothetical decay of the corresponding isolated level in an empty manifold, even to the extent of displaying hyperfine quantum beats in the hole alignment. The Doppler-resolved kinetics reflect a competition between the speed-dependent rotational energy transfer rates, which tend to cool the velocity distribution of the hole, and velocity-changing collisions, which tend to rethermalize the velocity distribution. The observations are of relevance to speed-dependent effects in pressure broadening, but measured under Doppler-limited pressure conditions. Elastic depolarization contributes significantly to the observed signals at low rotational states, negligibly so at high J. A strongly J-dependent contribution to the relaxation kinetics due to small amounts of the photolytic precursor cannot be neglected when extracting the rare-gas-dependent rate coefficients from the observed kinetics. Some qualitative differences are thereby found with previously published energy transfer studies on He or Ar + CN ($\tilde{X}$, v=2) by Fei, et al. [*J. Chem. Phys.* **100**, 1190 (1994); *Chem. Phys. Lett.* **232**, 547 (1995)].

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

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